Supplementary Information

Experimental and First-Principles DFT Study on the Electrochemical Reactivity of Garnet-Type Solid Electrolytes with Carbon

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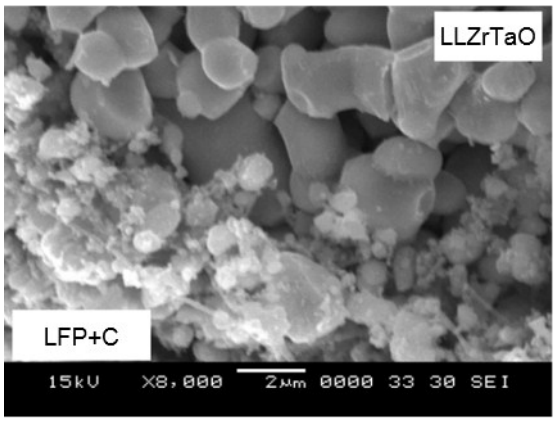

Figure S1. SEM image taken at the LFP+C - LLZrTaO interface.

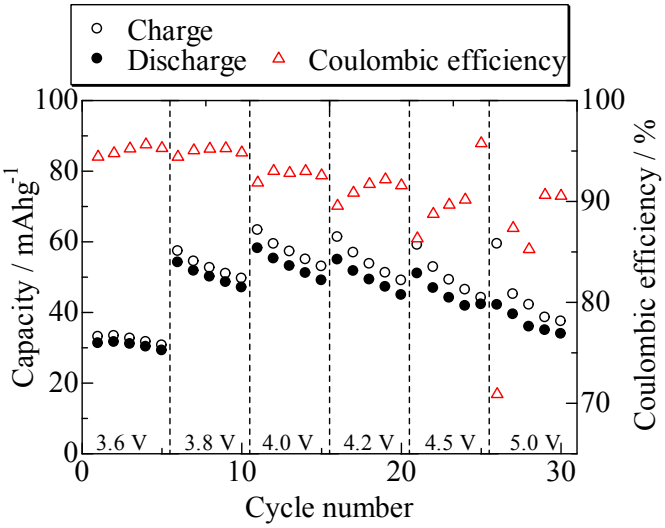

Figure S2. Figure. Cycle characteristics for the Li/LLZrTaO/(LFP+C) cell at various cutoff voltage (0.05 C rate).

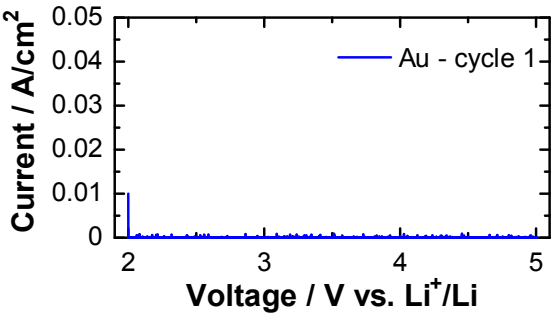

Figure S3. Cyclic voltammogram of a Li/LLZrTaO/Au cell.

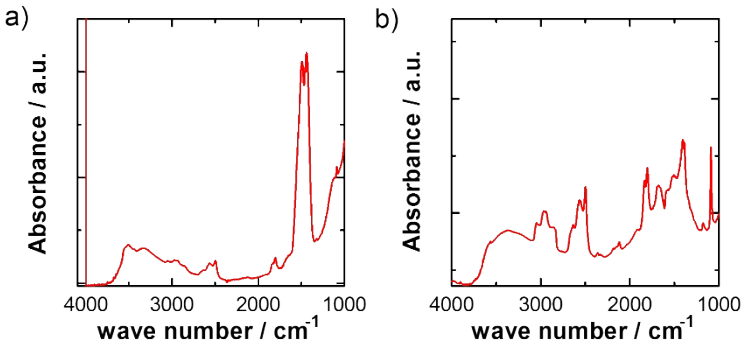

Figure S4. FTIR spectra for a) fresh LLZrTaO and b) Li_2CO_3.

Table S1. DFT-calculated decomposition potential of various non-carbon-related reactions. Thermodynamically stable constituent compounds are referred from the Materials Project database.[1]

Reaction formula	DFT-calculated decomposition potential (V)
$4\ Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12} = 0.50\ Li_2O_2 + 3\ Li_6Zr_2O_7 + 2\ Li_3TaO_4 + 6\ La_2O_3 + Li$	3.90
$Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12} = 0.5\ Li_2O_2 + 0.75\ Li_6Zr_2O_7 + 0.5\ La_3TaO_7 + 0.75\ La_2O_3 + Li$	3.21
$0.308\ Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12} = 0.5\ Li_2O_2 + 0.231\ La_2Zr_2O_7 + 0.154\ La_3TaO_7 + Li$	3.05
$0.4\ Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12} = 0.5\ Li_2O_2 + 0.3\ La_2Zr_2O_7 + 0.2\ Li_3TaO_4 + 0.3\ La_2O_3 + Li$	3.05
$0.5\ Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12} = 0.5\ Li_2O_2 + 0.375\ La_2Zr_2O_7 + 0.25\ Li_5TaO_5 + 0.375\ La_2O_3 + Li$	3.08
$1.091\ Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12} = 0.50\ Li_2O_2 + 0.818\ Li_6Zr_2O_7 + 0.182\ LiTa_3O_8 + 1.636\ La_2O_3 +$	3.96
$1.333\ LLi_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12} = 0.5\ Li_2O_2 + 1.0\ Li_6Zr_2O_7 + 0.667\ LiTaO_3 + 2\ La_2O_3 + Li$	3.73
$0.316\ Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12} = 0.5\ Li_2O_2 + 0.237\ La_2Zr_2O_7 + 0.053\ LiTa_3O_8 + 0.237\ La_2O_3 +$	3.21
$0.333\ Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12} = 0.5\ Li_2O_2 + 0.25\ La_2Zr_2O_7 + 0.167\ LiTaO_3 + 0.250\ La_2O_3 + Li$	3.10
$Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12} = 0.5\ Li_2O_2 + 0.75\ Li_6Zr_2O_7 + 0.167\ LaTa_3O_9 + 1.417La_2O_3 + Li$	3.71
$Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12} = 0.5\ Li_2O_2 + 0.75\ Li_6Zr_2O_7 + 0.071\ LaTa_7O_{19} + 1.464La_2O_3 + Li$	3.97
$Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12} = 0.5\ Li_2O_2 + 0.75\ Li_6Zr_2O_7 + 0.5\ LaTaO_4 + 1.25\ La_2O_3 + Li$	3.48
$0.308\ Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12} = 0.5\ Li_2O_2 + 0.231\ La_2Zr_2O_7 + 0.051\ LaTa_3O_9 + 0.205\ La_2O_3 +$	3.28
$0.308\ Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12} = 0.5\ Li_2O_2 + 0.231\ La_2Zr_2O_7 + 0.022\ LaTa_7O_{19} + 0.22\ La_2O_3 +$	3.24
$0.308\ Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12} = 0.5\ Li_2O_2 + 0.231\ La_2Zr_2O_7 + 0.154\ LaTaO_4 + 0.154\ La_2O_3 + L$	3.13
$2\ Li_7La_3Zr_2O_{12} = 0.5\ Li_2O_2 + 2\ Li_6Zr_2O_7 + 3\ La_2O_3 + Li$	3.59

Reference:

1 A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder and K. A. Persson, *APL Materials*, 2013, **1**, 011002.